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Development of an active tritium sampler for discriminating chemical forms without the use of combustion gases in a fusion test facility

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A new type of active tritium sampler that can discriminate between chemical forms in a fusion test facility without the use of combustion gases was developed. The proposed tritium sampler was operated using water vapour instead of combustion gases. To test the operation and performance of the device when water vapour is used, we evaluated the catalytic oxidation properties, and the evaporation and collection of water vapour under actual sampling conditions. The properties of the added water mass and the operation temperature of catalysts in the proposed sampling system were then determined. Thereafter, we carried out air sampling for tritium monitoring. The levels of tritium concentration measured by the proposed tritium sampling system were similar to the values measured by the conventional sampling system. Our findings show that the proposed tritium sampling system without combustion gases is a good replacement for the conventional tritium sampling system in a fusion test facility.

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1. Introduction

Tritium is a radioactive isotope of hydrogen that emits beta rays with a maximum energy of 18.6 keV, decays to ^3He , and has a half-life of 12.3 y (DOE HANDBOOK, 2008). Tritium forms naturally through cosmic ray interactions with the atmosphere. The annual production rate is estimated to be 70 PBq, and the resulting tritium inventory in nature is calculated to be 1–1.3 EBq. Furthermore, tritium is produced in nuclear power reactors during the fission of heavy nuclei and during neutron interactions with coolant materials. The amount of tritium discharged from nuclear facilities from 1995 to 1997 is estimated to be 43 PBq (UNSCEAR, 2000). Further, tritium is also a by-product of atmospheric nuclear tests. Based on the production rate and the total fusion and fission yield of nuclear tests, the production of tritium during nuclear tests is estimated to be 185 EBq. Since the tritium produced during atmospheric nuclear tests decays over time, the present level is 19 EBq (Bennett, 2002). In the 1970s, the atmospheric tritium concentration was more than 100 mBq/m³ as a result of nuclear testing during the 1950s and 1960s, but it has now exponentially decreased to less than 1/10 of its peak.

Nuclear fusion, for which deuterium (D) and tritium (T) are utilized as fuel, is considered a key energy source. These hydrogen isotopes can easily permeate metal walls under elevated temperatures. The leakage of tritium from fuel processing systems in a fusion facility cannot be entirely stopped. For safety against tritium and radiation management, tritium is removed from the air in facility rooms by tritium removal systems. In accordance with radiation management regulations, part of this tritium is released into the environment from a stack. As a monitoring technique, a tritium sampler is used to accumulate the extremely low levels of tritium within a given period. Koarashi et al. (Koarashi, 2004 and 2006), monitored total tritium levels using an active sampler at a fuel reprocessing plant.

Measuring and monitoring the different forms of tritium is preferred as the biological effects of tritium depend on its chemical form. In tritium samplers that discriminate chemicals, combustion gases such as hydrogen and methane are required to obtain water samples sufficient for liquid scintillation counting because atmospheric concentration levels of H_2 and CH_4 are very low at about 0.53 ppm (Novelli, 1999, Price, 2007) and 1.75 ppm (Dlugokencky, 2003), respectively. In the radiation control area of a fusion test facility, the tritium sampler has to operate without any supervision. Therefore, it is imperative that the system functions safely when combustion gases are used. With these considerations, we have developed a continuous tritium sampler that uses water vapour instead of combustion gases, based on the work of Kakiuchi et al (Kakiuchi, 2007). We also evaluated the efficiency of water evaporation from a vial, and the oxidation performance of the catalysts under very low concentrations of hydrogen and methane in relation to temperature in this work. In addition, we present the monitoring results for actual stack air sampling.

2. Experimental apparatus and method

2.1. Tritium sampling and activity measurement

A tritium sampler system was installed in the machine room of the building in which the fusion test device was housed and it was connected to the sampling line in the stack. The fusion test device has been operated since the last decade to study the plasma physics (Komori, 2010). It has not, however, been used to conduct plasma experiments using hydrogen isotope gases like deuterium. While naturally formed tritium is present, artificial tritium produced by fusion reactions is absent in the fusion test device building.

A schematic diagram and photographs of the developed tritium sampler are shown in Figs. 1 and 2, respectively. The sampler has two paths for continuous sampling; the operational path switches

after a given period of time. Air sampling is done at a flow rate of less than 2000 (std) cm³/min for a few weeks. The total amount of air collected was approximately 4–20 m³.

Molecular sieves (Wako Pure Chemical Industries, LTD.) of 3A-type one-sixteenth inch pellet were used. The dry molecular sieve was packed with approximately 550 g of absorbent. Tritium in the chemical form of HTO was collected in the first column of water vapour in the sampled air. After drying the air using molecular sieves, tritium free water vapour was added by evaporating tritium free water to the sampled air. Twenty to forty grams of tritium free water was added to an acryl vial and set in the water cooling column. The temperature of cooling water was controlled and maintained between -10 °C and 10 °C. Tritium in the chemical form of HT was then converted into HTO in an oxidation furnace with metal honeycombs supporting the platinum catalyst (Tanaka Kikinzoku Industry, Pt: 6 g/L, ϕ 25mm and 150 mmL, cell density: 300 CPSI) at 100 °C. The HTO formed was then collected together with tritium free water in the second molecular sieve column. Lastly, the tritium free water vapour was added by evaporating the tritium free water to the sampled air in the same manner as in the case of HT collection. The residual tritium in chemical form of CH₃T was then converted into HTO by an alumina supported palladium catalyst (NE Chemcat, ND-101, Pd: 5 g/L, packed weight: 290 g, column shape: ϕ 40 mm (O.D.) and 300 mmL) heated to about 350 °C. The HTO was collected together with tritium free water in the third molecular sieve column. The water collected in the molecular sieve columns was desorbed at a temperature of 400 °C and then recovered using a cold trap of about 2 °C under an N₂ gas purge at a rate of 1 L/min for 3.5 h.

To measure the tritium activity, 65 mL of the recovered water from the HTO collection column and 65 mL of liquid scintillator Ultima-Gold LLT (Perkin Elmer Co. Ltd.) were mixed in a 145 mL Teflon vial. Ten millilitres of the water recovered from each of the HT and CH₃T collection

columns were mixed with 10 mL of liquid scintillator in 20 mL Teflon vials. Background samples in 145 and 20 mL vials were prepared using tritium free water. After leaving these samples for a few days in a low background liquid scintillation counter LB-7 (Hitachi - Aloka Co. Ltd.), the tritium activity was determined for a total of 1500 min per sample.

2.2. Control of evaporation of water

The cylindrical water vial was set in the water cooling column to control the evaporation temperature, as shown in Fig. 2. The rate of evaporation from the cylindrical water surface was estimated by following the theoretical evaporation equation derived from natural convection condition [Ueda, 1964]:

$$\begin{aligned} w_{loss} &= 3.2 \times r^{1.75} \times (e_s - e) \times t \times 10^{-3}, \quad r < 10 \text{ cm} \\ &\approx 3.2 \times r^{1.75} \times e_s \times t \times 10^{-3} \end{aligned} \quad (1)$$

where, w_{loss} [g/h] is the rate of evaporation from the water surface, r [cm] is the radius of the cylindrical water vial, t [h] is operation time, e_s [hPa] is saturated water vapour pressure at a given temperature, and e [hPa] is the atmospheric water vapour pressure. In this case, the value of “ e ” can be ignored because the sampling gas passing through the molecular sieves column is in an extremely dry condition (less than 0.1 Pa). According to Eq. (1), the amount of evaporation from the cylindrical water vial is proportional to the surface area of the water vial, and sampling time and saturated water vapour pressure act as functions of ambient temperature.

2.3. Apparent oxidation efficiencies of catalysts under extremely low concentration of hydrogen and

methane

Oxidation performance was evaluated using a flow-type fix bed catalyst reactor (Tanaka, 2009). The gas flow diagram of the experimental apparatus is shown in Fig. 3. The shapes of the metal honeycomb catalyst supported the platinum for hydrogen oxidation was $\phi 25$ mm, 150 mmL and the catalyst density was 6 g/L. The cell density of the honeycomb catalyst was 300 cells per square inch (CPSI). The alumina supported palladium catalyst for methane oxidation was filled in the glass column which was the shape of $\phi 25$ mm, 180 mmL. The weight of catalyst was 100 g. To examine the oxidizing catalysts using very low concentrations of hydrogen and methane under wet conditions, the room air was fed using an air pump, into a test piece catalyst set in an electric furnace. The feed flow rate varied from 500 to 2000 cm³/min. The temperature of the electric furnace was increased stepwise using a programmable temperature controller, and the temperature was kept at a constant value for a period of 2.5 h. The catalyst could be heated up to about 350 °C. The temperature of the electric furnace was measured by a thermocouple. The concentrations of hydrogen and methane in the sampling air were 2.38 ppm and 1.73 ppm, respectively. Additionally, the sampled air had a dew point of around 1 °C. The process gases were sampled at the inlet and outlet of the catalyst bed and their concentrations were analysed using a gas chromatograph (GTR Tech, G2700TF) with a Trace Reduction Detector (TRD) (Kawano, 2003, 2004) for hydrogen and a Flame Ionization Detector (FID) for methane. The detection limits of these detectors were approximately 10 ppb. The conversion rate of oxidation, C [-], was defined by the following equation:

$$C = 1 - \frac{C_{out}}{C_{in}}, \quad (2)$$

where C_{in} is the gas concentration at the inlet of the catalyst bed and C_{out} is the gas concentration at the outlet of the catalyst bed.

3. Results and Discussion

3.1. Evaporation of water

Figure 4(a) shows the rate of evaporative loss from the water vial as a function of the radius of the cylindrical vial under various temperature conditions with an operational time of 168 h. The rate of evaporative loss corresponded to the evaporation rate of water from the water vial. The radii of the test vials were 8.5 mm and 21.5 mm. The evaporation rate of water was dependent on the radius of the cylindrical vial and could therefore be controlled by the surface area of the vial. In the actual tritium sampler, the larger vial with a radius of 21.5 mm was treated with an addition of water vapour. Figure 4(b) shows the rate of evaporative loss from the water vial as a function of the water temperature in the water cooling column under various operational times. The radius of the test vial was 21.5 mm. The evaporation rate of the water seems to be dependent on the water temperature; however, the evaporation rate could not be controlled sufficiently when temperatures exceeded 0 °C. It may be difficult to maintain water temperature in the vial using an indirect temperature control method. The water evaporation rate is independent of temperature and remained constant over a wide range of temperatures, making the temperature of the cooling water unimportant for the sampling operation. Figure 4(c) shows the amount of evaporative loss from the water vial as a function of collection time. The temperature of the cooling water was set at 0 °C and the radius of the test vial was 21.5 mm. The evaporation rate was proportional to the collection time. According to these results, air sampling was conducted to obtain enough water weight during the collection time, taking the ambient temperature and the absolute humidity in the air into consideration.

3.2. Oxidation performance of catalysts

The performance of two types of catalysts and their oxidation properties were evaluated under extremely low hydrogen and methane concentrations. Figure 5(a) shows the relationships between the temperature and hydrogen conversion rate for the platinum honeycomb type catalyst at 1 L/min. The flow rate less than 1 L/min is corresponding to that of the normal sampling operation. The hydrogen gas was completely oxidized above 100 °C. Figure 5(b) shows the relationships between the flow rate and hydrogen conversion rate at 100 °C. Although the conversion rate of hydrogen decreased slightly as the flow rate increased, it was more than 0.97 at 2 L/min. On the other hand, methane was not oxidized in the evaluated range of temperature and flow rate.

Figure 6(a) shows the relationships between the temperature and the conversion rate of methane for the palladium catalyst where the flow rate was 1 L/min. Methane gas was oxidized at a conversion rate of 1 above 250 °C. Figure 6(b) shows the relationships between the flow rate and methane conversion rate at 350 °C. The conversion rate did not depend on the flow rate in the range of 2 L/min. The conversion rate of methane was 1 at 2 L/min even though the test catalyst volume was less than the volume of the catalyst column in the actual sampler. This catalyst can be considered since the methane oxidation performance is sufficient at temperatures higher than 250 °C.

3.3. Collection of water vapour by the sampler system

The results of water collection under various actual operational conditions are summarized in Table 1. The amount of water weight in the first column for HTO depends on the absolute humidity in the sampled air. Thus, the weight of the collected water varied with the total sampling volume and the season. The amount of water evaporation from each water vial for the columns of hydrogen and methane could be controlled by controlling the sampling time and cooling temperature. Then, the evaporation water from the water vial was collected using the molecular sieve column. The table

shows that the collected water mass was proportional to the evaporation water mass. The water vapour recovery efficiency, which is the ratio of water evaporation mass of the vial and collected water mass in the molecular sieves column, is also shown in Table 1. The water recovery efficiency of both the molecular sieves columns of HT and CH₃T are indicated to be more than 0.96. Thus, the water addition system for the tritium sampling was successful and proved to be a useful method.

3.4. Results of tritium concentration monitoring in the stack

Tritium sampling in the stack was carried out from July 2012 to November 2015. Prior to this, the fusion test facility had not been handling tritium; thus the air in the stack corresponded to the environmental atmosphere. The tritium concentrations in each chemical form and the absolute humidity are indicated in Fig. 7. The detection limits of tritium concentration were dependent on the sampling volume of the sampler and the sample volume of the liquid scintillation counter. The data below the detection limit were omitted from Fig. 7. Humidity in the building was controlled by air conditioning units, thus suppressing the absolute humidity range in the stack at a level lower than the outdoor humidity range. The atmospheric tritium water vapour (HTO) concentration varied with humidity due to the multiplying effect of the absolute humidity as shown in Fig 7(a) and (b). The seasonal variation of HTO concentration had similar tendencies as previous results reported using conventional sampling systems (Tanaka, 2015). The concentrations of HT and CH₃T did not vary clearly with season. HT and CH₃T could not be detected at small sampling volumes because the amount of HT and CH₃T in the atmosphere was very low. Thus, we are unable to discuss the seasonal variation of the tritium concentrations of HT and CH₃T.

The tritium concentrations at Toki are summarized in Table 2, where we compare the results from the published data concerning conventional sampling systems and the ones obtained in this study

by using the proposed sampling system. The data from the conventional sampling systems show the atmospheric tritium concentration in the environment at Toki (Uda, 2011, Tanaka, 2015). The ranges of tritium concentrations are similar for both the conventional system and the proposed system. Thus, our findings indicate that the proposed sampling system has the same performance as the conventional sampling system. The proposed sampling system without combustion gases can be used instead of the conventional sampling systems in a fusion test facility.

4. Conclusion

A new type of tritium sampler using water vapour instead of combustion gases to discriminate between the three chemical forms of tritium was proposed for fusion test facilities. To develop the active tritium sampler, the performance of water evaporation, the catalytic oxidation of hydrogen and methane under extremely low concentrations, and the collection of water vapour by the proposed sampling system were evaluated. The amount of water evaporation, operational temperature of catalysts, and the balance of water mass in the proposal sampling system were determined. Thereafter, we sampled and monitored the air in a stack. The range of variation in the tritium concentration in each case using the proposed sampling system was similar to the concentration range when using the conventional sampling system. Therefore, it can be said that the new type of tritium sampling system that functions without combustion gases can replace the conventional tritium sampling system in the fusion test facilities.

From the viewpoint of radiation management in fusion test facilities, a continuous sampling operation in the stack is required for tritium monitoring. The proposed sampling system has two sampling lines and collection columns so the line can be switched after a given period of time. For the construction of background tritium database before tritium production by deuterium (D)–D reaction in

the facility, continuous tritium monitoring in the stack by the proposal sampling system will be continued.

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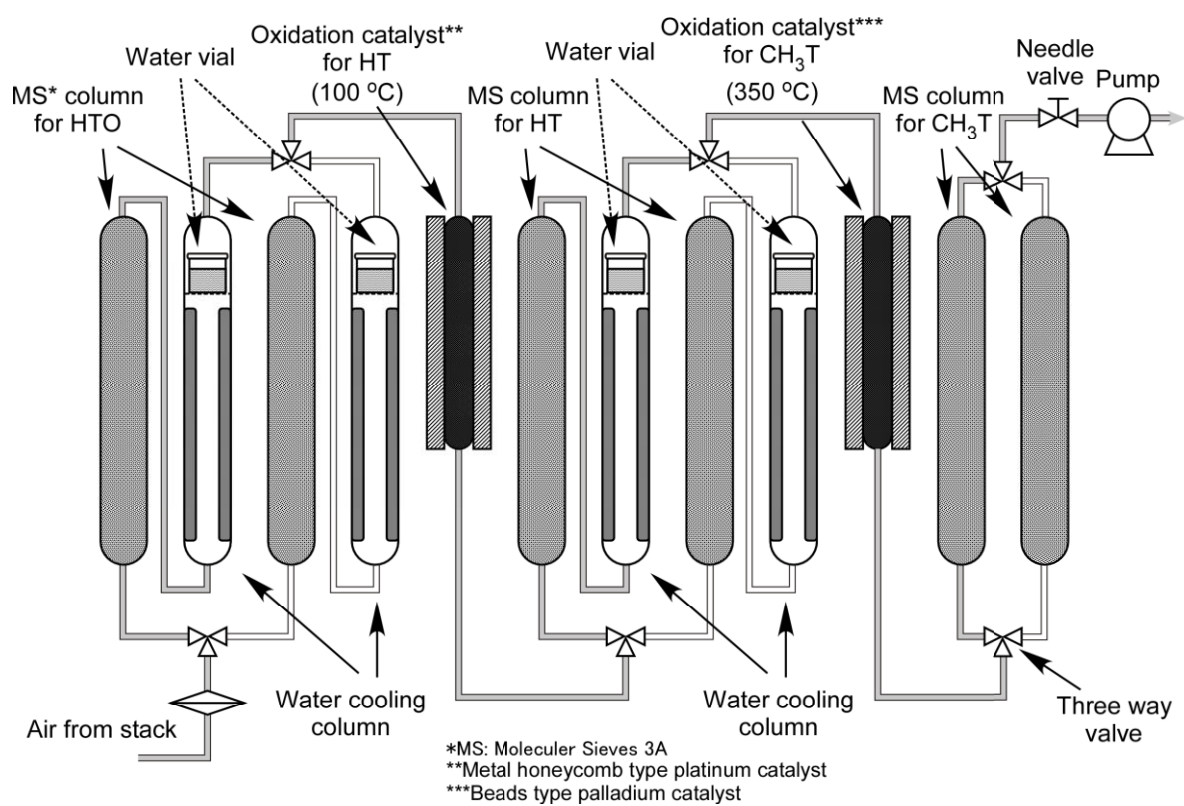


Fig. 1 Schematic diagram of the active tritium sampling system.



Fig. 2 Photos of the active tritium sampling system without combustion gases and setup of the cylindrical water vial

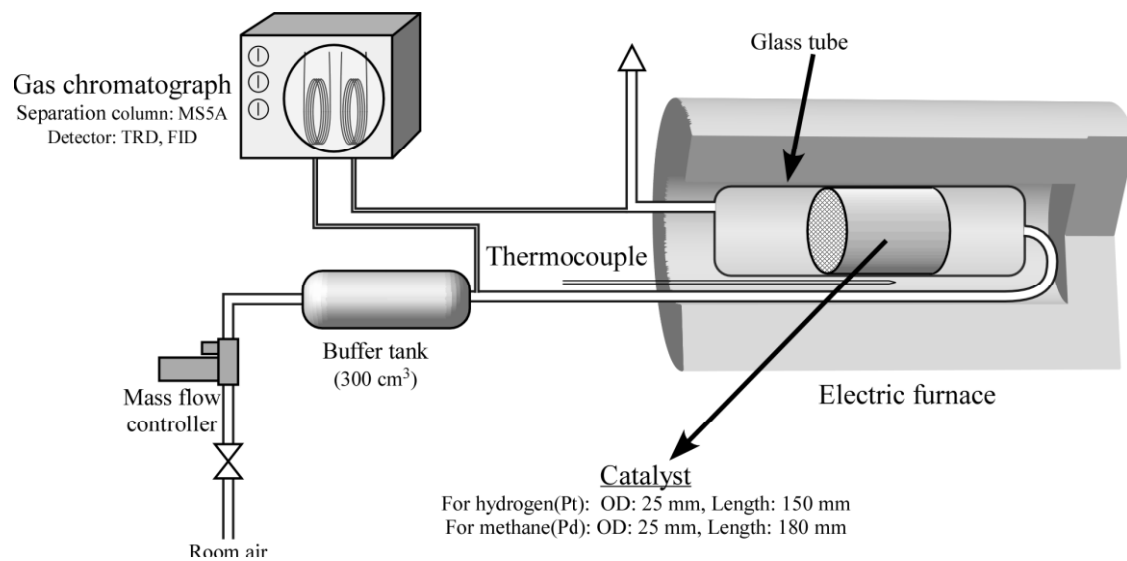


Fig. 3 Schematic diagram of the catalyst oxidation efficiency test system

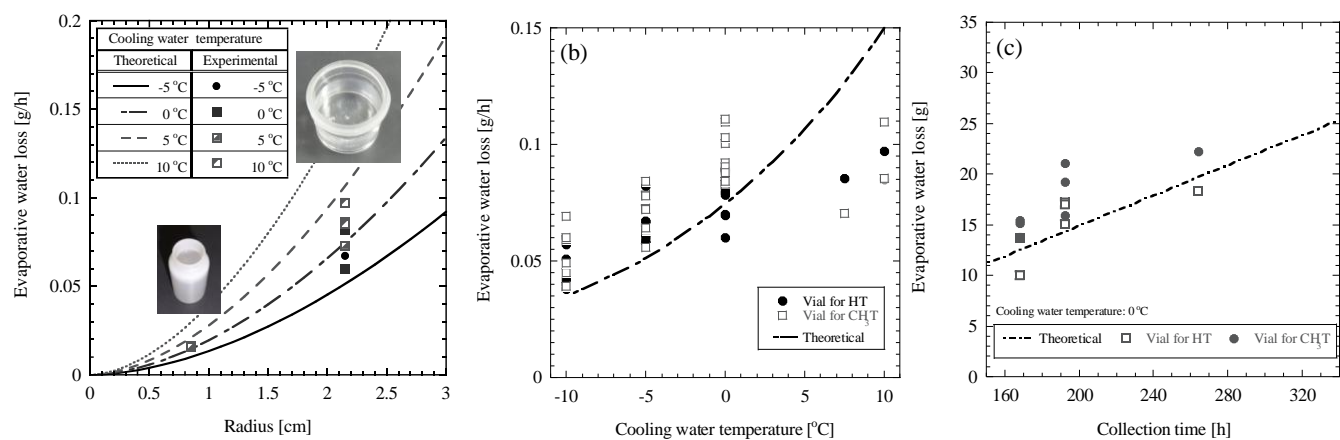


Fig. 4 Evaporation of water in the vial under various operation conditions; (a) dependency of the radius of the vial on the rate of evaporation, (b) dependency of the cooling water temperature on the rate of evaporation, and (c) dependency of collection time on the amount of evaporation.

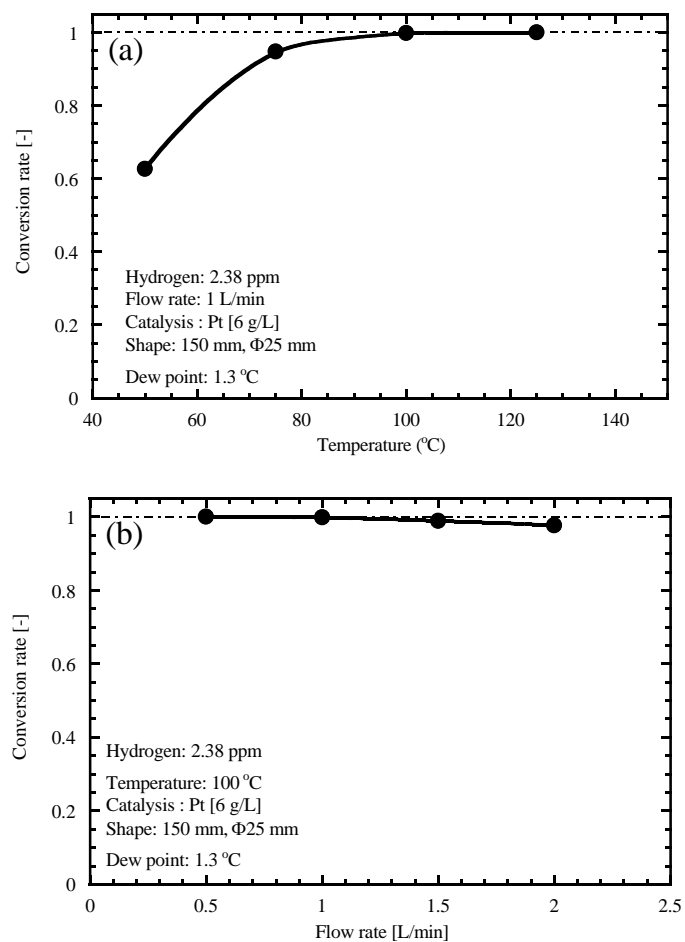


Fig. 5 Oxidizing efficiency of platinum catalyst for hydrogen gas:

(a). Temperature dependency at the flow rate of 1 L/min, (b). Flow rate dependency at the temperature of 100°C

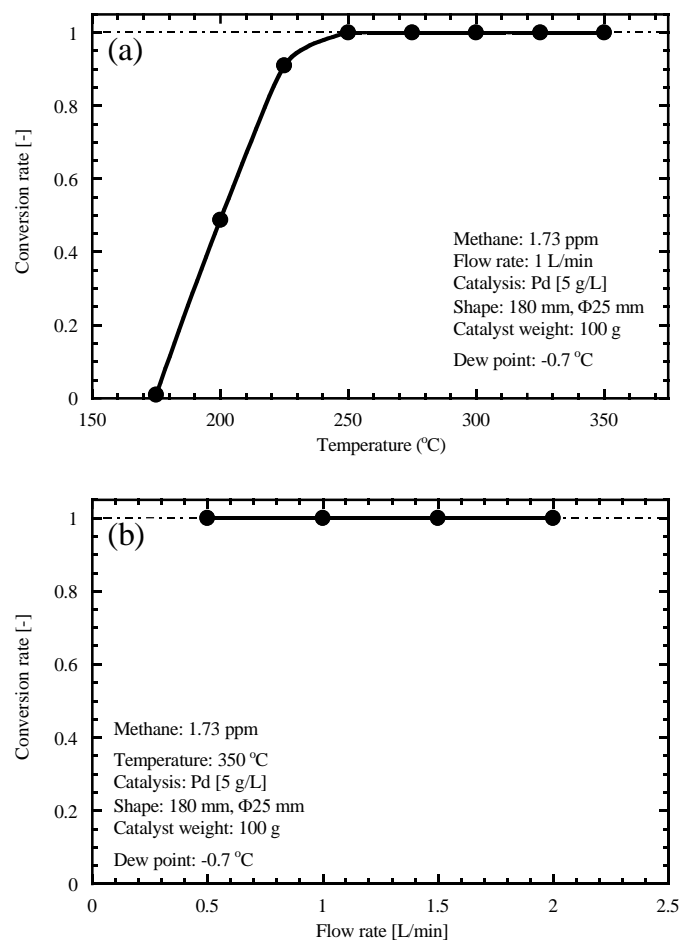


Fig. 6 Oxidizing efficiency of palladium catalyst for methane gas:

(a). Temperature dependency at the flow rate of 1 L/min, (b). Flow rate dependency at the temperature of

350°C

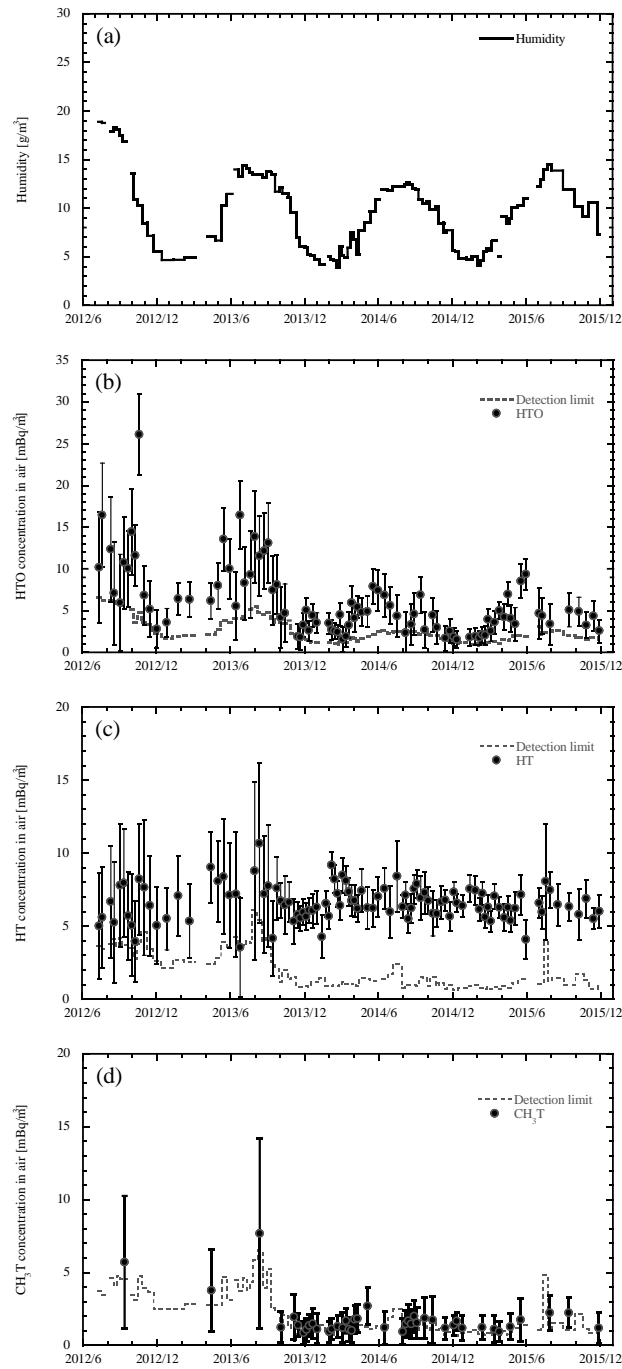


Fig. 7 Tritium concentrations of different chemical forms and absolute humidity:

(a) absolute humidity, (b) HTO, (c) HT, and (d) CH_3T

Table 1. Operational results of water collection under various actual operation conditions

Run No.	Collection term			Collection time	Collection volume	Absolute humidity	Cooling temperature	MS column for HTO: collecting water	Evaporation water to MS column for HT (A)	MS column for HT: collecting water (a)	Water recovery rate: a/A	Evaporation water to MS column of CH ₃ T (B)	MS column for CH ₃ T: collecting water (b)	Water recovery rate: b/B
				[h]	[m ³]	[g/m ³]	[°C]	[g]	[g]	[g]	[-]	[g]	[g]	[-]
1	2012/8/7	-	2012/8/15	192	4.15	18.0	0	92.42	17.03	17.07	1.00	21.08	21.26	1.01
2	2012/8/15	-	2012/8/23	192	4.96	18.3	0	90.78	17.22	16.85	0.98	15.94	15.91	1.00
3	2012/8/23	-	2012/8/31	192	5.09	18.1	0	91.97	15.07	15.13	1.00	19.3	19.68	1.02
4	2012/8/31	-	2012/9/7	168	4.05	17.5	0	71.04	13.75	13.38	0.97	15.48	14.84	0.96
5	2012/9/7	-	2012/9/17	264	6.03	16.8	0	101.48	18.42	18.45	1.00	22.22	22.27	1.00
6	2012/9/28	-	2012/10/5	168	4.60	13.6	-5	62.36	11.27	11.24	1.00	13.13	13.13	1.00
7	2012/10/5	-	2012/10/15	240	6.11	10.9	-5	66.41	14.04	13.94	0.99	15.22	15.26	1.00
8	2012/10/15	-	2012/10/25	240	5.94	10.3	-5	61.06	14.68	14.48	0.99	17.36	17.37	1.00
9	2012/10/25	-	2012/11/8	336	8.01	8.5	-5	67.97	21.07	21.05	1.00	19.13	18.94	0.99
10	2012/11/8	-	2012/11/22	336	8.62	7.1	-10	61.26	17.06	17.07	1.00	19.61	19.73	1.01
11	2012/11/22	-	2012/12/13	504	10.68	5.5	-10	58.57	19.39	19.4	1.00	19.65	19.78	1.01
12	2012/12/13	-	2013/1/10	672	17.07	4.7	-10	79.69	25.78	25.75	1.00	30.32	30.43	1.00
13	2013/1/10	-	2013/2/7	672	16.37	4.7	-10	76.62	26.96	26.99	1.00	25.94	26.04	1.00
14	2013/2/7	-	2013/3/7	672	18.53	5.0	-10	91.85	28.58	28.44	1.00	33.19	33.21	1.00
15	2013/4/4	-	2013/4/25	504	13.79	7.1	-10	97.19	28.71	28.72	1.00	35.19	34.83	0.99
16	2013/4/25	-	2013/5/9	329	7.72	6.6	-10	51.29	19.6	19.67	1.00	19.81	19.9	1.00

MS: Molecular sieves

Table 2. Comparison of the tritium concentrations obtained from a conventional sampler and the new proposed sampler

Sampler type	Tritium concentration at Toki			Sampling term
	HTO [mBq/m ³]	HT [mBq/m ³]	CH ₃ T [mBq/m ³]	
Conventional sampler	2 ~ 23	6 ~ 11	0.5 ~ 3	2004 ~ 2012
New proposed sampler	1.5 ~ 26	3.6 ~ 10.7	0.9 ~ 7.7	2012/7 ~ 2015/11